PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2004-010701

(43)Date of publication of application : 15.01.2004

(51)Int.Cl. C08L 23/04
C08J 5/18
C08J 9/26
C08K 3/00
C08K 5/00
C08K 7/00

(21)Application number : 2002-164114

(22)Date of filing : 05.06.2002

(71)Applicant : ASAHI KASEI CORP

(72)Inventor : AKASHI KAZUO

(54) POLYOLEFIN MEMBRANE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a highly heat-resistant polyolefin membrane incorporated with a small amount of a filler, and to provide a porous polyolefin membrane produced by making said membrane porous.

SOLUTION: The polyolefin membrane contains 1-30 wt.% of one or more kinds of particles selected from particles ≤100 nm in mean size and laminar mineral particles. The porous polyolefin membrane is produced by exposing the above membrane to a solvent for polyolefin to swell the membrane followed by extracting and removing the solvent to make the membrane porous.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]
This invention relates to the polyolefine porosity film which porosity-ized the polyolefine film and this especially whose thermal resistance improved about the polyolefine film which uses polyethylene as a principal component.
[0002]
[Description of the Prior Art]
Since the melting point of polyethylene is comparatively low, it is excellent in fabrication nature, and acidity and its resistance over alkaline chemicals are large, and excellent also in dampproofing. The polyolefine film which carried out fabrication of the polyolefine which what fabricated the polyolefine which uses polyethylene as a principal component on the film of the quality of nonporous is widely used as dampproof wrapping etc. using this description, and uses polyethylene as a principal component to the porosity-ized film or the hollow filament is used for the battery separator, the filter, etc.
[0003]
However, if polyethylene is heated, it will be easy to deform, compared with the film with which the melting point of a polyamide, polyester, etc. fabricated the high polymer, thermal resistance is low, and the polyolefine film which uses polyethylene as a principal component is in the inclination for the temperature used to be restricted.
As a means for improving the thermal resistance of polyethylene, adding inorganic fillers, such as talc, is performed widely. However, since the irregularity of the front face of the polyolefine film becomes large or extending to a high scale factor becomes difficult by mixing an inorganic filler in large quantities, it is difficult to fabricate polyolefine film, such as a film and a hollow filament, from the polyolefine which uses as a principal component the polyethylene which mixed a lot of inorganic fillers.

[0004]
Since the melting point of polyethylene is low, the thin film which, on the other hand, porosity-ized polyolefine which uses polyethylene as a principal component has the features of quality[of nonporous]-izing, at low temperature, and is used as a separator of a cell taking advantage of these features.
That is, when a cell sets in the overcharge condition, or is heated and the temperature inside a cell rises, in order to quality[of nonporous]-ize the film which porosity-ized polyolefine which uses polyethylene as a principal component at comparatively low temperature, it discovers the function which intercepts the current inside a cell and controls the rise of the temperature inside a cell.
[0005]
In recent years, the cell of high energy density is called for with high-performance-izing and advanced features using a cell of a cellular phone or a notebook computer. When the temperature of a cell rises, even after quality[of nonporous]-izing and intercepting a current as a separator of the cell of such high

energy density, preventing maintaining a configuration, without carrying out the amniorrhexis to higher temperature, and the electrodes inside a cell contacting and short-circuiting is called for.
As an approach which make the amniorrhexis of the film which porosity-ized polyolefine which uses polyethylene as a principal component hard to carry out to higher temperature, using ultra high molecular weight polyethylene is proposed.
[0006]
Since the melt viscosity of ultra high molecular weight polyethylene is very high, it is difficult to manufacture the polyolefine film which uses ultra high molecular weight polyethylene as a principal component with the equipment which manufactures the polyolefine film which uses usual polyethylene as a principal component.
In order to manufacture the film which porosity-ized polyolefine which uses ultra high molecular weight polyethylene as a principal component, the approach (JP,5-54495,B) of mixing with a solvent the polyolefine which uses ultra high molecular weight polyethylene as a principal component, reducing viscosity, and fabricating on the film is performed.
A manufacturing facility becomes large-scale or these shaping approaches tend to become complicated [a production process], in order to use a lot of solvents.
[0007]
[Problem(s) to be Solved by the Invention]
Although the polyolefine film with which the amount of the filler added uses as a principal component the polyethylene of high thermal resistance which can be manufactured by few [and] simple manufacturing facilities was called for, there was nothing that satisfies this to this.
This invention aims at offering the polyolefine film which uses as a principal component the polyethylene with which addition mixing of a small amount of filler is carried out, and high thermal resistance is obtained, and the polyolefine porosity film which uses as a principal component the polyethylene which porosity-ized this.
[0008]
[Means for Solving the Problem]
The result of having inquired wholeheartedly in order that this invention person might solve said technical problem, The polyolefine film with which mean particle diameter mixed one or more sorts of particles chosen from a particle 100nm or less and a stratified mineral particle 30 or less % of the weight 1% of the weight or more shows high thermal resistance to the polyolefine which uses polyethylene as a principal component. After contacting this polyolefine film to the solvent of polyolefine and making it swell, it finds out that the polyolefine film porosity-ized by carrying out extract removal of the solvent turns into heat-resistant high porosity-ized polyolefine film etc., and it came to make this invention.
[0009]
That is, this invention is as follows.
1. Polyolefine film which uses as principal component polyethylene which contains one or more sorts of particles chosen from particles stratified mineral particle and whose mean particle diameter are 100nm or less 30 or less % of the weight 1% of the weight or more.
2. Polyolefine porosity film which carries out extract removal and comes [porosity]-izing [a solvent] after contacting polyolefine film which uses as principal component polyethylene which contains one or more sorts of particles chosen from particles stratified mineral particle and whose mean particle diameter are 100nm or less 30 or less % of the weight 1% of the weight or more to solvent of polyolefine and making it swell.
[0010]
[Embodiment of the Invention]
Hereafter, it explains concretely focusing on the desirable mode of this invention, especially this invention.
The polyolefine film of this invention is polyolefine film which uses polyethylene as a principal component, and the polyethylene used for this invention is the blend object of the copolymers of the homopolymer of ethylene and ethylene, and olefins, such as a propylene, a butene, a hexene, and octene,

and these copolymers, and an ethylene homopolymer.
It is desirable that the melt flow rate measured by the approach indicated by K7210 of JIS out of these polyethylene uses 2g / polyethylene for 10 or less minutes, and it is more desirable that a melt flow rate uses 1g / polyethylene for 10 or less minutes further.
[0011]
Polypropylene, a polyamide, denaturation polyphenylene ether, etc. can be included in the polyolefine film which uses the polyethylene of this invention as a principal component out of these polyethylene.
As for the rate of the polyethylene contained in the polyolefine film which uses the polyethylene of this invention as a principal component, it is desirable that it is 99 or less % of the weight 60 % of the weight or more to a polyolefine film total amount, and it is more desirable that it is [70 more % of the weight or more] 99 or less % of the weight.
[0012]
the particle used for this invention has a stratified mineral particle and independent mean particle diameter in the particle chosen from the particles which are 100nm or less -- or two or more sorts are combined and it is used.
The particle whose mean particle diameter used for this invention is 100nm or less is the inorganic substance particle and organic substance particle whose mean particle diameter is 100nm or less. If mean particle diameter exceeds 100nm, the reinforcement of the polyolefine film which added the particle will tend to become small.
[0013]
The particle whose mean particle diameter is 100nm or less For example, the particle of inorganic oxide metallurgy group oxides, such as oxidization silicon, an alumina, and titanium oxide, It is the particle of carbon constituents, such as a particle of polyolefines, such as polystyrene, and the polymer of immiscible nature, fullerene, and a nano carbon tube, etc. When using the porosity-ized polyolefine film as a battery separator, as for the particle to be used, it is desirable that it is insulation, and its oxidation silicon particle and alumina particle which performed hydrophobing processing for the front face of a particle by the alkyl group are more more desirable still. 1nm or more of minimums of particle diameter is 3nm or more still more preferably preferably.
[0014]
The mean particle diameter of this invention is the value of the mean particle diameter called for by the mean-particle-diameter measuring method generally called a specific-surface-area measuring method, and is the value of the mean particle diameter called for by 6/(Srho) of formulas using the specific surface area (S) of a particle and the consistency (rho) of a particle which were measured by the gas adsorption method currently generally called the BET adsorption method.
The stratified mineral particle used for this invention is the mineral particle which has lamellar crystal structures, such as a smectite, a kaolin, and a mica, a stratified mineral particle may be used for it as it is, and the stratified mineral particle which inserted and made oligomer organic between crystal layers may be used for it by mixing with the stratified mineral particle and the monomer which exchanged for alkyl ammonium ion etc. cations, such as sodium contained in a crystal, and made them organic, and carrying out a polymerization.
[0015]
As for the total amount of the particle whose stratified mineral particle and mean particle diameter which are contained in the polyolefine film of this invention are 100nm or less, it is desirable that it is 30 or less % of the weight more than per % of the weight to a polyolefine film total amount, and it is more desirable that it is [1 more % of the weight or more] 20 or less % of the weight.
It is difficult to acquire the effectiveness that the thermal resistance of the polyolefine film improves, when the content rate of a particle total amount is less than 1 % of the weight, and when exceeding 30 % of the weight, the reinforcement of the polyolefine film tends to become [the aggregate of a particle] being easy to generate small.
[0016]
On the polyolefine film of this invention, in order to make homogeneity distribute a particle in

polyolefine, the acid denaturation polyolefine to which an organic acid and polyolefines, such as fatty-acid metal salts, such as fatty-acid amide compounds, such as fatty acids, such as stearic acid and an erucic acid, and octadecanamide, an erucic-acid amide, calcium stearate, and zinc stearate, and a maleic acid, were made to react may be added.
When using a fatty acid, a fatty-acid amide compound, and a fatty-acid metal salt, the addition rate to polyolefine is 0.1 - 4 % of the weight preferably 0.05 to 5% of the weight. When using acid denaturation polyolefine, the addition rate to polyolefine has 5 - 30 desirable % of the weight, and it is 5 - 20 % of the weight more preferably.
[0017]
Moreover, to the polyolefine used by this invention, various additives, such as an antioxidant and a nucleating agent, may be added if needed.
The polyolefine film of this invention can be manufactured by performing press forming and extension processing, after carrying out melting kneading of the polyolefine which uses as a principal component the polyethylene which mixed the particle at 30 or less % of the weight of a rate 1% of the weight or more.
Thus, after contacting the polyolefine film of the obtained quality of nonporous to the solvent of polyolefine and making it swell, it can be made the porosity-ized polyolefine porosity film by the solvent which does not dissolve polyolefine washing, and removing a solvent and drying.
[0018]
The polyolefine constituent with which melting kneading of polyolefine and the particle was carried out can be manufactured by the approach of heating and kneading polyolefine and a particle to the temperature more than the melting point of polyolefine using mixed equipments, such as a kneader and a twin screw extruder.
The polyolefine constituent obtained by carrying out heating kneading of polyolefine and the particle can be fabricated the shape of the shape of a sheet, or tubing, and in the shape of a hollow filament. It inserts into the metal plate which cooled the polyolefine constituent by which heating kneading was carried out, and quenches. For example, fabricate in the shape of a sheet, or Fabricate in the shape of a sheet by taking over with a cooling roller what extruded the polyolefine constituent which carried out heating kneading using the extruder which attached the sheet forming die at the tip from the sheet forming die, or By extruding the polyolefine constituent which carried out heating kneading using the extruder which attached the tubular die and the hollow filament spinning port at the tip from a tubular die or a hollow filament spinning port, it can fabricate the shape of tubing, and in the shape of a hollow filament.
[0019]
In this invention, the mixture of the shape of a sheet, the polyolefine fabricated tubular or in the shape of a hollow filament, and a particle can be extended.
Extension of a sheet-like moldings is performed using coincidence extension equipments, such as serial extension equipment which combined extension equipments, such as a roll drawing machine and a tenter, and these, or a coincidence 2 shaft tenter.
In the case of a tubular moldings, it can carry out by the approach of enclosing a compressed air with the interior of a tubular moldings, and extending in the shape of a tube. In the case of a tubular moldings, you may carry out combining tube-like extension and sheet-like extension.
[0020]
From the point of securing the reinforcement of the polyolefine film obtained, as for draw magnification, it is desirable that they are 3 or more times, and it is more desirable that they are further 4 or more times.
It is desirable that extension of this invention is performed at with a melting point melting point [of polyolefine / melting point +10 degrees C or less of -40 degrees C or more] temperature, and it is more desirable to be further carried out at the temperature below the melting point of the melting point the polyolefine of -20 degrees C or more of polyolefine.
A pinhole is easy to be included in the thin film which it is easy to fracture polyolefine by extension

when extension is performed at the temperature which is less than the melting point of -40 degrees C of polyolefine, and is obtained also when not fracturing.
[0021]
On the other hand, when extension is performed at the temperature exceeding the melting point of +10 degrees C of polyolefine, dispersion in thickness will tend to become [the tensile strength of the porous film obtained] small large.
The polyolefine porosity film with which this invention was porosity-ized can be manufactured by the approach of making the solvent which dissolves or fuses alternatively the amorphous part of the polyolefine film of the quality of nonporous obtained as mentioned above contacting, and making a hole forming, for example, as it is the following, it can be performed.
[0022]
The porosity-ized polyolefine porosity film can be manufactured by drying, after washing by liquid (b) which solvent (b) which dissolves or fuses the amorphous part of polyolefine alternatively is heated, and it puts into a cistern, it takes out from a cistern after being immersed in solvent (b) of a cistern and making it swell the polyolefine film of the quality of nonporous, and there are solvent (b) and compatibility, and does not dissolve polyolefin resin and removing solvent (b).
[0023]
independent [from a hydrocarbons /, such as paraffin oil, /, low-grade fatty alcohol, and low-grade aliphatic series ketone, a nitrogen content organic compound, the ether, a glycol, low-grade aliphatic series ester, a silicone oil, etc.] as solvent (b) -- or it can combine and use. Although the desirable temperature of solvent (b) is based on polyolefine or the class of solvent (b), in the case of polyethylene, the temperature of 100 degrees C - 140 degrees C is desirable, for example.
If processing temperature is high, in order to be able to do short and to maintain the reinforcement of resin after being porosity-ized, the shorter one of the processing time is [the processing time] desirable.

[0024]
As liquid (b), it is desirable to use ketones, such as non-chlorine content fluorine system organic solvents, such as low-boiling point hydrocarbons, such as a hexane, the hydro FURORO ether, and hydro fluorocarbon, and a methyl ether ketone.
In order to adjust the magnitude and the number of a hole of polyolefine porosity film which are obtained and which were porosity-ized, the polyolefine film immersed in solvent (b) can be extended, and the polyolefine porosity film porosity-ized after washing and drying by liquid (b) can also be extended further.
[0025]
Moreover, when the polyolefine film which was immersed in solvent (b) and swollen curtains, in order to remove sag, the rate which takes over the polyolefine film from the cistern filled with solvent (b) may be made larger than the rate sent to a cistern.
[0026]
This invention is explained based on an example.
The evaluation approach of the physical properties of the polyolefine film in an example is as follows.
(a) Thickness
It measured using the OZAKI MFG dial gage "PEACOK No.25" (trade name).
(b) Usual state Korean floor heater prickle reinforcement
The radius of curvature at a tip attached the needle which is 0.5mm, performed the **** trial at the **** rate of 2mm/second, and the temperature of 23 degrees C, and made the maximum **** load **** reinforcement (N) at the compression tester made from a KATO tech "KES-G5" (trade name).
[0027]
(c) High Korean floor heater prickle reinforcement
After being immersed in the silicone oil (the Shin-Etsu Chemical make, trade name "KF-96-10CS") which heated even to predetermined temperature what sandwiched the film with the bore of 13mm, and two washers made from stainless steel of 25mm of appearances, and stopped four perimeters with a clip,

**** reinforcement (N) was measured by the same approach as the above (b).
[0028]
(d) Porosity
It asked for the volume of a sample from thickness and area, and mass was measured and it asked for porosity using the following formula. The value calculated by count from the polyolefine, the consistency of a particle, and the blending ratio of coal which were used was used for the consistency.
Porosity (%) =(1- (mass/consistency) / volume) x100
(e) Air permeability
It measured using the gar rhe type air permeability meter based on JIS P-8117.
[0029]
(f) Hole lock out temperature and amniorrhexis temperature
drawing 1 (A) - (C) -- a hole -- the schematic diagram of the measuring device of lock out temperature and amniorrhexis temperature is shown. Drawing 1 (A) is the block diagram of a measuring device. 1 is the polyolefine porosity film and 10micromNi foil in thickness, and 3A and 3B of 2A and 2B are glass plates. 4 is an electric resistance measuring device (Ando Electric LCR meter "AG4311" (trade name)), and is connected with nickel foil (2A, 2B). 5 is a thermocouple and is connected with the thermometer 6. 7 is a data collector and is connected with the electric resistance measuring device 4 and the thermometer 6. 8 is oven and heats the polyolefine porosity film.
[0030]
If it furthermore explains to a detail, the regular electrolytic solution sinks into the polyolefine porosity film 1, and as shown in drawing 1 (B), it is fixed in the form where only MD was stopped on the Teflon (trademark) tape (shadow area), on nickel foil 2A. As shown in drawing 1 (C), nickel foil 2B leaves a 15mmx10mm part, and is masked on the Teflon (trademark) tape (shadow area). nickel foil 2A and nickel foil 2B are piled up in a form which sandwiches the fine porosity film 1, and nickel foil of two sheets is further put with glass plates 3A and 3B from the both sides. The glass plate of two sheets is fixed by inserting with a commercial clip. Temperature and electric resistance are continuously measured using the equipment shown in drawing 1 (A).
[0031]
In addition, the temperature up of the temperature is carried out at the rate of 2 degrees C / min, and an electric resistance value is measured by 1kHz alternating current. It is defined as temperature in case the electric resistance value of the fine porosity film 1 amounts to 103 ohms in hole lock out temperature. When carrying out the temperature up of the temperature to amniorrhexis temperature further, it is defined as the temperature when the electric resistance value of the fine porosity film 1 falling, and amounting to 103ohms or less again.
In addition, the regular electrolytic-solution presentation is as follows.
solvent: -- propylene carbonate / ethylene carbonate / butyl lactone =1/1/2 volume % solute: -- with the above-mentioned solvent, hoe lithium fluoride was melted so that it might become the concentration of one mol/l.
[0032]
[Example 1]
A consistency the high density polyethylene of 0.95 g/cm3 for 0.3g / 10 minutes 78 % of the weight, [the melting point] [134 degrees C and a melt flow rate] the hydrophobic silica particle (Shin-Etsu Chemical --) from which mean particle diameter was processed by 7nm, and the front face was processed by the methyl group The trade name "X-130" was mixed 20% of the weight, stearic acid was mixed at 2% of the weight of a rate, using the Oriental energy machine factory PURASUTO mill C mold, temperature was set as 200 degrees C, the rotational frequency was set as 50rpm, and heating mixing of this mixture was carried out for 10 minutes.
After picking out the mixture which carried out heating mixing from the PURASUTO mill and cooling to ordinary temperature, it inserted between the metal plates of two sheets, and compressed by pressure 10MPa using the heat.press machine set as the temperature of 200 degrees C, and the film with a thickness of 100 micrometers was created.

It was 0.51Ns when the high Korean floor heater prickle reinforcement of the created film was measured at 130 degrees C.
[0033]
[Example 2]
Instead of the hydrophobic silica particle of an example 1, the carbon number of an alkyl group created the film with a thickness of 100 micrometers on the same conditions as an example 1 from the mixture of the rate of 5 % of the weight of synthetic mica made organic 93 % of the weight of high density polyethylene using the synthetic mica (CO-OP CHEMICAL, trade name "SOMASHIFU MAE") made organic by the dialkyl dimethyl ammonium ion which is 14 to 18, and 2 % of the weight of stearic acid.
It was 0.39Ns when the high Korean floor heater prickle reinforcement of the created film was measured at 130 degrees C.
[0034]
[The example 1 of a comparison]
The high density polyethylene and stearic acid which were used in the example 1 were mixed at 98 % of the weight and 2% of the weight of a rate, and the film with a thickness of 100 micrometers was created on the same conditions as an example 1.
When the high Korean floor heater prickle reinforcement of the created film is measured at 130 degrees C, compared with the film which added the particle of an example 1 or an example 2, the value of high Korean floor heater prickle reinforcement is small, and it turns out to be 0.25 Ns that the reinforcement in the elevated temperature of the polyethylene film is large by addition of a particle.
[0035]
[Example 3]
The high density polyethylene, the same hydrophobic silica particle, and same stearic acid as an example 1 were mixed at same rate as an example 1, and the film with a thickness of 800 micrometers was created on the same conditions as an example 1. Both directions in every direction extended the obtained film by 6 times as many draw magnification as this at the temperature of 128 degrees C using the biaxial-stretching machine (made in the Iwamoto factory), and the thin film was created.
It dried in the 24 more hour ordinary temperature which washed the thin film which is immersed in the cistern which filled the liquid paraffin whose temperature is 131 degrees C about the obtained thin film for 1 minute, it was made to swell, and was swollen by the methyl ethyl ketone, and removed the liquid paraffin, and the porosity-ized thin film was created.
the obtained thin film which was porosity-ized -- thickness -- 16 micrometers and porosity -- 42% and air permeability -- 460 seconds and usual state Korean floor heater prickle reinforcement -- 4.1 Ns and a hole -- lock out temperature was 133 degrees C, and heat-resistant temperature was 170 degrees C.
[0036]
[Example 4]
The hydrophobic silica particle of an example 3 was replaced with the alumina particle (C.I. Kasei, trade name "Nanotech") whose mean particle diameter is 30nm, and was mixed to high density poly ECHIRE and stearic acid at same rate as an example 3, and the film with a thickness of 800 micrometers was created on the same conditions as an example 3. Both directions in every direction extended the obtained film by 6 times as many draw magnification as this at the temperature of 128 degrees C using the biaxial-stretching machine (made in the Iwamoto factory), and the thin film was created.
It dried in the 24 more hour ordinary temperature which washed the thin film which is immersed in the cistern which filled the liquid paraffin whose temperature is 131 degrees C about the obtained thin film for 1 minute, it was made to swell, and was swollen by the methyl ethyl ketone, and removed the liquid paraffin, and the porosity-ized thin film was created.
the obtained thin film which was porosity-ized -- thickness -- 15 micrometers and porosity -- 47% and air permeability -- 500 seconds and usual state Korean floor heater prickle reinforcement -- 4.0 Ns and a hole -- lock out temperature was 133 degrees C, and heat-resistant temperature was 170 degrees C.
[0037]
[The example 2 of a comparison]

From the mixture of the high density polyethylene used for the example 1 of a comparison, and stearic acid, the film with a thickness of 800 micrometers was created on the same conditions as the example 1 of a comparison.
Extension and porosity-ization were performed on the same conditions as an example 3, and the porosity-ized film was created.
The obtained film which was porosity-ized is film 132 degrees C and whose amniorrhexis temperature 2.7N and hole lock out temperature are [thickness / 15 micrometers and porosity / 37% and air permeability] 141 degrees C for 700 seconds and **** reinforcement, its amniorrhexis temperature is lower than the film which added the particle of an example 3 or an example 4, and it turns out that the amniorrhexis temperature of the porosity-ized film is high by addition of a particle.
[0038]
[Effect of the Invention]
The polyolefine film of this invention is the polyolefine film of high thermal resistance with few additions of a filler, and polyolefine film of high thermal resistance which porosity-ized this polyolefine film, and is very useful as a battery separator, a filter, etc.
[Brief Description of the Drawings]
[Drawing 1] (A) -- a hole -- it is the whole schematic diagram showing the configuration of the equipment which measures lock out temperature, and (B) is a sectional view in nickel foil (2A) side of (A), and (C) is a sectional view in nickel foil (2B) side of (A).
[Description of Notations]
1: Polyolefine porosity film
2A, a 2B:nickel foil
3A, 3B: Glass plate
4: Electric resistance measuring device
5: Thermocouple
6: Thermometer
7: Data collector
8: Oven

[Translation done.]